DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to optical amplification glass. In particular, it is related with the optical amplification glass which can be amplified in a broadband to light with a wavelength of 1.4-1.5 micrometers.

[0002]

[Description of the Prior Art]It consists of core glass and clad glass for the purpose of the application to the light amplifier in an optical fiber communications system, and development of the optical amplification glass with which the rare earth element was added is furthered as this glass for core glass. On the other hand, in order to correspond to diversification of the communications service upon which it will count in the future, the wavelength-multiplex-optical-telecommunications method (WDM) which aims at expansion of transmission capacity is proposed. In WDM, transmission capacity becomes large, so that the number of channels of wavelength multiplexing increases.

[0003]The optical amplification glass with which Er (erbium) was added as suitable glass for the optical amplification of a C band (wavelength: 1530-1560 nm) or an L band (wavelength: 1570-1600 nm) conventionally, The optical amplification glass with which Tm (thulium) was added as suitable glass for the optical amplification of an S^+ band (wavelength: 1450-1490 nm) and S band (wavelength: 1490-1530 nm) is proposed, respectively.

[0004]Excitation light enters into Tm addition optical amplification glass, the light, i.e., the optical signal, which should be amplified, and an optical signal is amplified using the stimulated emission transition of Tm. The wavelength of excitation light is 1.0-1.6 micrometers typically, when performing excitation by the rise conversion method. Tm addition optical amplification glass is used usually fiber-izing it.

[0005]

[Problem(s) to be Solved by the Invention]In Tm addition optical amplification glass, optical amplification of an S^+ band and S band is performed using the stimulated emission transition between $^3H_4$-$^3F_4$. However, under $^3H_4$ level, level $^3H_5$ which about 4300 cm^{-1} Separates and approaches exists. The multi-phonon relaxation in said stimulated emission transition increases for this contiguity level $^3H_5$, radiation relaxation decreases, and there is a possibility that luminous efficiency, therefore the rate of optical amplification may fall as a result.

[0006]As Tm addition optical amplification glass, the optical amplification glass with which Tm was added by fluoride glass, for example is proposed. Compared with oxide glass, there is the strong point in which multi-phonon relaxation is small in fluoride glass. However, low (typically 320 ** or less), glass transition point T_g of fluoride glass had a possibility that it might be damaged thermally, when the intensity of excitation light became large. Since Vickers hardness H_V of fluoride glass was low (typically 2.4GPa), when it was easy to attach a crack and it fiber-ized, there was a possibility that the crack might become a cause and might fracture.

[0007]As optical amplification glass with which Tm was added by fluoride glass. The presentation of a mol % display For example, ZrF_4:52.53%, BaF_2: 20.20%, LaF_3:3.03%, AlF_3: 4.04%, NaF : Tm is added 1.19% by the mass percentage display by the matrix glass which is 20.20%, Tm addition fluoride glass ZBLAN in which the peak wavelength of 200 ** and an emission spectrum is 1452 nm, and T_g is [the half breadth] 76 nm is known (Applied Optics, 39 (27), 4979-4984 (2000)).

[0008]As optical amplification glass with which Tm was added by the tellurite glass. The presentation of a mol % display For example, TeO_2:75%, ZnO:10%, Although Tm is added 1.23% by the mass percentage display by the matrix glass which is O:15% of Na_2 and Tm addition tellurite glass in which the peak wavelength of an emission spectrum is 1458 nm, and the half breadth is 114 nm is known, The T_g is 295 ** low (Applied Optics, 39 (27), 4979-4984 (2000)).

[0009]PbO:56-mol % and Bi_2O_3:27-mol %, To the matrix glass which consists of Ga_2O_3:17-mol %. 0.01%, 0.05%, or the glass (Tm addition PbO-Bi_2O_3-Ga_2O_3 glass) added 1.5% is indicated for Tm by the mass percentage display (Applied Optics, 34 (21), 4284-4289 (1995)). The annealing point of said matrix glass and Knoop hardness are 319 ** and 2.2GPa, respectively (Phys.Chem.Glasses, 27,119-123 (1986)). Even if it may consider that an annealing point is equal to T_g and adds Tm to 1.5%, it is thought that there is no big change in T_G. That is, T_g of said Tm addition PbO-Bi_2O_3-Ga_2O_3 glass is about 320 ** too, and has a

possibility that said thermally damaging may happen.

[0010]In the case of optical glass, if what is become a low value 0.4 to 1.3 GPa rather than H_V (the encyclopedia of glass, 352 pages, Asakura Publishing, 1985 issue) is taken into consideration, Knoop hardness, It is thought that H_V of said Tm addition PbO-Bi_2O_3-Ga_2O_3 glass is in the range of 2.6 - 3.5GPa, and it can never be said that it is high. T_g and H_V of this invention are high, and it aims at offer of optical amplification glass which can amplify the light of an S^+ band and S band.

[0011]

[Means for Solving the Problem]this invention is optical amplification glass with which 0.001 to 10% of Tm is added by matrix glass by mass percentage display -- this matrix glass -- Bi_2O_3 -- 15-80-mol % -- optical amplification glass which contains and contains GeO_2 is provided.

[0012]

[Embodiment of the Invention]As for T_g of the optical amplification glass of this invention, it is preferred that it is not less than 360 **. This is because there is a possibility that the temperature of glass may become high locally and optical amplification may become glass is thermally damaged by T_g in less than 360 **, and optical loss increases as a result, and insufficient when a laser beam with large intensity is used as excitation light for optical amplification. Not less than 400 ** is not less than 420 ** especially preferably more preferably.

[0013]As for H_V of the optical amplification glass of this invention, it is preferred that they are 3.6 or more GPa. In less than 3.6 GPa, there is a possibility of becoming easy to fracture when it fiber-izes. 3.7 or more GPa is 4.0 or more GPa especially preferably more preferably.

[0014]Tm is added in order to give an optical amplification function to the matrix glass in this invention. The rate of optical amplification falls [the addition (Tm addition) of a mass percentage display of Tm when matrix glass is made into 100%] at less than 0.001%. It is 0.05% or more more preferably 0.01% or more. At more than 10%, vitrification becomes difficult or the rate of optical amplification falls on the contrary for concentration quenching. It is 0.5% or less more preferably 1% or less.

[0015]Next, mol % is only displayed as % and the ingredient of the matrix glass in this invention is explained below. Bi_2O_3 is an essential ingredient. In less than 15%, the rate of optical amplification falls or the content carries out phase splitting. It is not less than 35% not less than 30% especially preferably not less than 25% still more preferably not less than 20% more preferably not less than 15.5%. At more than 80%, it devitrifies at the time of fiber processing to which vitrification becomes difficult, or T_g becomes low too much. It is 48% or

less 55% or less especially preferably 60% or less 70% or less preferably.

[0016]GeO_2 is network former and indispensable. As for the content of GeO_2, it is preferred that it is 5 to 80%. In less than 5%, vitrification becomes difficult or there is a possibility of devitrifying at the time of fiber processing. It is not less than 25% most preferably not less than 20% especially preferably not less than 15%. There is a possibility that the rate of optical amplification may fall or devitrify at the time of fiber processing, at more than 80%. It is 55% or less most preferably 60% or less especially preferably 75% or less.

[0017]Although Ga_2O_3 is not indispensable, in order to enlarge the wavelength interval from which a profit is acquired, or in order to control the devitrification at the time of fiber processing, it may contain to 30%. There is a possibility that a crystal may deposit at the time of glass production, and the transmissivity of glass may fall, at more than 30%. It is 25% or less preferably. As for the content, when it contains Ga_2O_3, it is preferred that it is 0.5% or more. It is not less than 5% most preferably not less than 3% especially preferably 1% or more.

[0018]Although CeO_2 is not indispensable, in order to control that Bi_2O_3 in glass composition returns into glass melting, deposits as metal bismuth, and reduces the transparency of glass, it may contain to 10%. There is a possibility that coloring of yellow or orange may become strong, the transmissivity of glass may fall, and a background loss [in / vitrification becomes difficult or / excitation light wavelength or optical signal wavelength] may increase, at more than 10%. It is 0.3% or less especially preferably 0.5% or less more preferably 1% or less. As for the content, when it contains CeO_2, it is preferred that it is 0.01% or more. It is 0.1% or more especially preferably 0.05% or more more preferably. As for the content of CeO_2, it is preferred to consider it as less than 0.15% and it is more preferred not to contain CeO_2 substantially to avoid decline in the transmissivity of glass.

[0019]Contain Ga_2O_3 or CeO_2 and Bi_2O_3, It is preferred that sum total $Bi_2O_3+GeO_2+Ga_2O_3+CeO_2$ of the content of GeO_2, Ga_2O_3, and CeO_2 is not less than 70%. It is more preferred to contain GeO_2 for Bi_2O_3 and to contain CeO_2 for Ga_2O_3 0.1 to 0.3% 0.5 to 25% 15 to 60% 15 to 48%. It is more preferred to contain GeO_2 for Bi_2O_3 and to contain CeO_2 for Ga_2O_3 0.1 to 0.3% 5 to 25% 25 to 60% 15 to 48%.

[0020]The matrix glass in this invention by the mol % display of the following oxide basis. 15 to 80% of Bi_2O_3, 5 to 80% of GeO_2, 0 to 30% of Ga_2O_3, 0 to 10% of CeO_2, 0 to 10% of WO_3, 0 to 20% of TeO_2, 0 to 30% of $aluminum_2O_3$, Li_2O 0-10%, Na_2O 0-20%, K_2O 0-20%, The thing become essential, 0 to 20% of ZnO, 0 to 20% of MgO, 0 to 20% of CaO, 0 to 20% of SrO, 0 to 20% of BaO, 0 to 10% of TiO_2, 0 to 10% of ZrO_2, 0 to 10% of SnO_2, ** et al., is preferred.

[0021]Since Bi_2O_3, GeO_2, Ga_2O_3, and CeO_2 were explained previously, ingredients other than these four ingredients are explained below. Although WO_3 is not indispensable, in order to enlarge the wavelength interval from which a profit is acquired, it may contain to 10%. There is a possibility that the rate of optical amplification may fall, at more than 10%.

[0022]Although TeO_2 is not indispensable, in order to increase the rate of optical amplification, it may contain to 20%. There is a possibility that a crystal may deposit at the time of glass production, and the transmissivity of glass may fall, at more than 20%. It is 5% or less more preferably 10% or less. As for the content, when it contains TeO_2, it is preferred that it is 1% or more. It is not less than 2% more preferably.

[0023]Although aluminum$_2O_3$ is not indispensable, in order to control the devitrification at the time of fiber processing, it may contain to 30%. There is a possibility that a crystal may deposit at the time of glass production, and the transmissivity of glass may fall, at more than 30%. It is 15% or less especially preferably 20% or less more preferably. As for the content, when it contains aluminum$_2O_3$, it is preferred that it is 0.1% or more. It is not less than 2% especially preferably 1% or more more preferably.

[0024]As for the sum total of the content of Ga_2O_3, aluminum$_2O_3$, and TeO_2, it is preferred that it is 50% or less. There is a possibility that a crystal may deposit at the time of glass production, and the transmissivity of glass may fall, at more than 50%. It is 20% or less most preferably 25% or less especially preferably 30% or less. The sum total of said content is not less than 4% more preferably not less than 2%.

[0025]Although all Li_2O, Na_2O, and K_2O are indispensable, in order to control the devitrification at the time of fiber processing, it may contain to 10%, 20%, and 20%, respectively. Although all ZnO, MgO, CaO(s), SrO(s), and BaO(s) are indispensable, in order to control the devitrification at the time of fiber processing, it may contain to 20%, respectively. Although all TiO_2, ZrO_2, and SnO_2 are indispensable, in order to control the devitrification at the time of fiber processing, it may contain to 10%, respectively.

[0026]Although desirable matrix glass consists of the above-mentioned ingredient intrinsically, other ingredients may be contained in the range which does not spoil the purpose of this invention. As for the sum total of the content of an ingredient besides ** "", it is preferred that it is 10% or less.

[0027]An ingredient" besides aforementioned " is described below. In order to make glass formulation easy, or in order to control the devitrification at the time of fiber processing, Cs_2O, CdO, PbO, Y_2O_3, La_2O_3, etc. may be contained. Tb_2O_3, Dy_2O_3, Ho_2O_3, Yb_2O_3, etc. may be contained as a sensitizer. As for the content of each ingredient, when it contains Tb_2O_3,

Dy_2O_3, Ho_2O_3, or Yb_2O_3, it is preferred that it is 0.001% or more. It is 0.1% or more especially preferably 0.01% or more more preferably.

[0028]Since PbO has a possibility of reducing H_V, not containing substantially is preferred. Since SiO_2 or B_2O_3 has a possibility of increasing multi-phonon relaxation, it is preferred to contain neither substantially.

[0029]There is no restriction in particular about the method of producing the optical amplification glass of this invention. Mix and a raw material For example, a platinum crucible, a platinum-gold alloy crucible, an alumina crucible, It puts in a quartz crucible or an iridium crucible, and the optical amplification glass of this invention can be produced with the scorification which carries out the cast of the melt (melting glass) obtained by fusing in the air at 800-1300 ** to a predetermined mold. In order to decrease the moisture in glass and to control increase of multi-phonon relaxation, few things of the moisture of the melting atmosphere in said scorification are preferred, for example, its use of dry nitrogen, dry air, etc. is preferred.

[0030]The optical amplification glass of this invention may be produced with methods, for example, a sol gel process, gaseous phase vacuum deposition, etc., other than scorification, etc. Optical amplification glass fiber can be created by creating and fiber-izing preforming or fiber-izing it by the double crucible method based on the optical amplification glass of this invention which was carried out in this way and produced.

[0031]

[Example]The glass which added Tm of the quantity shown in the matrix glass shown in the column from Bi_2O_3 of a table to BaO by mol % display by mass percentage display at the column of Tm was produced. T_g and crystallization-starting-temperature T_x which were calculated by differential thermal analysis (DTA) are shown in a table (unit: **). H_V is also shown about Examples 1 and 5 (unit: MPa).

[0032]T_x is a temperature to which the exothermic peak accompanying crystallization begins to rise, and is the temperature of the rule of thumb from which crystallization begins. As for T_x-T_g, it is preferred that it is not less than 50 **. At less than 50 **, there is a possibility of devitrifying at the time of fiber processing. Not less than 130 ** not less than 70 ** is not less than 150 ** most preferably especially preferably.

[0033]About the glass of Example 1, it irradiated with light with a wavelength of 800 nm using the semiconductor laser diode (output: 1W), and the emission spectrum in the wavelength of 1300-1600 nm was measured by using PbS as a detector. A result is shown in drawing 1 by making luminescence intensity into an arbitrary unit. The light emission peak (half breadth: 122

nm) by transition of $^3H_4$->$^3F_4$ of Tm is accepted near the wavelength of 1470 nm. Therefore, optical amplification [in / for example / by the rise conversion method / an S^+ band (wavelength: 1450-1490 nm) and S band (wavelength: 1490-1530 nm)] is possible.

[0034]The half breadth deltalambda is 122 nm, and is larger than 76 nm of Tm addition fluoride glass illustrated previously, and 114 nm of Tm addition tellurite glass. Therefore, the wavelength interval from which a profit is acquired is large, and superior to Tm addition glass of these former as optical amplification glass. deltalambda was similarly measured about Examples 2-5, 10-13, and 24. A result is shown in a table (unit: nm).

[0035]

[Table 1]

	例1	例2	例3	例4	例5	例6
Bi_2O_3	42.8	32.2	36.5	35.6	32.2	20.2
GeO_2	35.6	26.95	30.55	32.35	26.95	54.45
Ga_2O_3	21.4	16.7	17.8	18.9	16.7	9.8
CeO_2	0.2	0.15	0.15	0.15	0.15	0.15
Al_2O_3	--	--	--	--	--	--
Na_2O	--	--	--	--	2.5	9.8
K_2O	--	5.0	3.0	2.0	2.5	10.0
ZnO	--	10.0	6.0	4.0	10.0	4.8
MgO	--	--	--	--	--	1.8
CaO	--	--	--	--	--	--
SrO	--	--	--	--	--	--
BaO	--	10.0	6.0	4.0	10.0	9.6
Tm	0.22	0.06	0.1	0.05	0.1	0.1
T_g	470	430	440	440	425	380
T_x	540	575	540	540	580	485
T_x-T_g	70	145	100	100	155	105
H_v	4.0	--	--	--	3.7	--
$\Delta\lambda$	122	126	124	120	134	--

[0036]

[Table 2]

	例7	例8	例9	例10	例11	例12
Bi_2O_3	20.0	21.85	21.35	15.95	28.55	15.95
GeO_2	25.95	67.15	72.05	50.35	59.95	46.65
Ga_2O_3	3.0	5.35	6.45	8.55	5.35	12.25
CeO_2	0.15	0.15	0.15	0.15	0.15	0.15
Al_2O_3	8.9	6.0	—	—	6.0	—
Na_2O	13.2	—	—	—	—	—
K_2O	—	—	—	5.0	—	5.0
ZnO	4.7	—	—	10.0	—	10.0
MgO	0.4	—	—	—	—	—
CaO	9.1	—	—	—	—	—
SrO	7.8	—	—	—	—	—
BaO	6.8	—	—	10.0	—	10.0
Tm	0.1	0.1	0.1	0.1	0.1	0.1
T_g	420	510	480	485	505	490
T_x	470	650	620	615	640	645
$T_x - T_g$	50	140	140	130	135	155
H_V	—	—	—	—	—	—
$\Delta\lambda$	—	—	—	134	118	133

[0037]

[Table 3]

	例13	例14	例15	例16	例17	例18
Bi_2O_3	32.2	37.45	32.2	32.2	36.9	31.3
GeO_2	26.95	21.7	26.95	21.95	16.95	26.17
Ga_2O_3	15.7	15.7	12.2	15.7	18.0	15.24
CeO_2	0.15	0.15	0.15	0.15	0.15	0.15
Al_2O_3	—	—	3.5	—	—	—
Na_2O	5.0	—	—	—	—	2.42
K_2O	—	5.0	5.0	6.0	6.0	2.42
ZnO	10.0	10.0	10.0	12.0	12.0	9.7
Ti_2O_3	—	—	—	—	—	2.9
BaO	10.0	10.0	10.0	12.0	12.0	9.7
Tm	0.1	0.1	0.1	0.1	0.1	0.1
$\Delta\lambda$	124	—	—	—	—	—
T_g	430	410	425	425	400	—
T_x	575	580	570	580	550	—
$T_x - T_g$	145	170	145	155	150	—

[0038]

[Table 4]

	例19	例20	例21	例22	例23	例24
Bi_2O_3	31.8	31.88	31.88	35.25	21.35	21.35
GeO_2	26.17	26.69	26.69	27.84	72.0	44.94
Ga_2O_3	15.24	15.57	15.57	13.0	0.6	8.6
CeO_2	0.15	0.15	0.15	0.15	0.15	0.15
Al_2O_3	–	–	–	–	6.0	–
Na_2O	2.42	2.47	2.47	2.58	–	–
K_2O	2.42	2.47	2.47	2.58	–	5.0
ZnO	9.70	9.89	9.89	10.3	–	9.98
TiO_2	–	–	–	–	–	–
ZrO_2	–	0.99	–	–	–	–
La_2O_3	2.9	–	0.99	–	–	–
BaO	9.7	9.89	9.89	10.3	–	9.98
Tm	0.1	0.1	0.1	0.1	0.1	0.06
$\Delta\lambda$	–	–	–	–	–	156
T_x	440	430	430	420	490	470
T_g	615	580	630	575	640	575
$T_x - T_g$	175	150	200	155	150	105

[0039]

[Effect of the Invention]According to this invention, even if it uses a laser beam with large intensity as excitation light, thermal damage does not take place easily, Even if it fiber-izes, it is hard to fracture, and optical amplification glass with possible and optical amplification of an S^+ band and S band and a big wavelength interval from which a profit is acquired is obtained, and the mass information transmission by a wavelength multiplexing transmission system becomes possible also in an S^+ band and S band.

[Translation done.]